Synthesis of a Photochromic Conjugated Polymer Incorporating Spirobenzopyran in the Backbone

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Abstract: Photochromic conjugated polymer with photochemically isomerizable spirobenzopyran (SP) moiety as part of the conjugated backbone was synthesized. Upon irradiation with UV light of 365 nm, a new absorption band appeared above 500 nm due to the formation of the merocyanine (MC) form, which corresponds to a highly conjugated structure.

Keywords: conjugation, cross-coupling, isomerizations, polymers, spiro compounds

π-Conjugated semi-conducting polymers represent a novel class of organic semi-conductive materials that have been intensively investigated because of their interesting optoelectronic properties and potential applications in several technologically important areas such as all-organic field-effect transistors, organic light-emitting devices, solar cells, photoconductive materials, nonlinear optical materials, and sensors.[1] Photochromism is a phenomenon associated with light-induced reversible isomerization of a molecular species between two isomeric forms having different absorption properties.[2] The spirobenzopyran family constitutes one of the most widely studied photochromic systems due to their ease of synthesis and potential applications in optical information storage and processing, molecular switching, memory devices, and other emerging technologies.[3] The photochromism of spirobenzopyran is associated with a reversible color change between the closed-ring (colorless) spiropyran (SP) structure and the open-ring (highly colored) merocyanine (MC) form.[4]

We have become interested in integrating the concept of photochromic systems and π-conjugated polymers to produce new organic semi-conductive polymers that may potentially exhibit photoswitchable optoelectronic properties. As evident from the literature on photochromic polymeric systems, the majority reported so far have photochromic units appended as side chains on a few class of readily accessible polymers such as poly(methyl methacrylates) (PMMA) and polystyrenes (PS).[5] There have been a few recent reports of photochromic backbone conjugated polymers as well.[6] In these works, the photochromes used were based on the 1,2-dithienylethene or related systems, by taking advantage of the facile photochemically allowed electrocyclic reactions. In this paper, we report our preliminary effort in the design and synthesis of a new spirobenzopyran-based polymer system with photochromic units incorporated in the backbone of a typical conjugated polymer, poly(*p*-phenylene ethynylene) (PPE). While typical photochromes such as derivatives of spirobenzopyran, 1,2-dithienylethene, and azobenzene have been frequently employed in a number of photochromic polymeric or dendritic systems,[4–6] the specific incorporation of spirobenzopyran units into part of the π-conjugated polymer backbone (rather than as moieties on the side chains) that would lead to a linear polymer capable of completing full conjugation along the polymer backbone in the merocyanine form is new. The general synthetic strategy leading to the spirobenzopyran-containing PPE (based on palladium-catalyzed cross-coupling) outlined in this paper should be readily applicable to the synthesis of other interesting conjugated polymers such as poly(3-alkylthiophenes) (PT), poly(*p*-phenylene vinylenes) (PPV) and poly(*p*-phenylenes) (PP) as well.

The synthesis of polymer **9** was carried out following the reaction sequences described in Schemes 1– 4. The two monomers needed for the palladium-catalyzed (Sonogashira cross-coupling) condensative polymerization are 1,4-diiodobenzene and bis(acetylene) **8**. The long alkoxy chains introduced on the aromatic rings in monomer **8** serve to increase the solubility of the resulting rigid rod-like segmented PPE polymer. It is noteworthy that a convenient protecting group (hydroxymethylethynyl group) for masking terminal acetylenic functionality was successfully used in the synthesis of various terminal acetylenes in this work, in good agreement with previous work reported by Godt and coworkers.[7] This masked protecting group can be deprotected under relatively mild conditions by simply stirring with a mixture of commercial manganese dioxide (20 equiv) and powdered potassium hydroxide (10 equiv) in dichloromethane or diethyl ether at room temperature. This condition is mild when compared to the conditions normally required for the deprotection of the 2-hydroxyprop-2-yl moiety where a strong base (NaOH, KOH, or NaH) in refluxing toluene or alcohol is used.[8] In addition, the corresponding acetylene starting material used (propargyl alcohol) is inexpensive when compared with the more commonly used silyl-substituted terminal acetylenes such as trimethylsilylacetylene or triisopropylsilylacetylene. In our case, an added advantage is that the separation and purification of all of the intermediates were made easier with the introduction of this polar acetylene-

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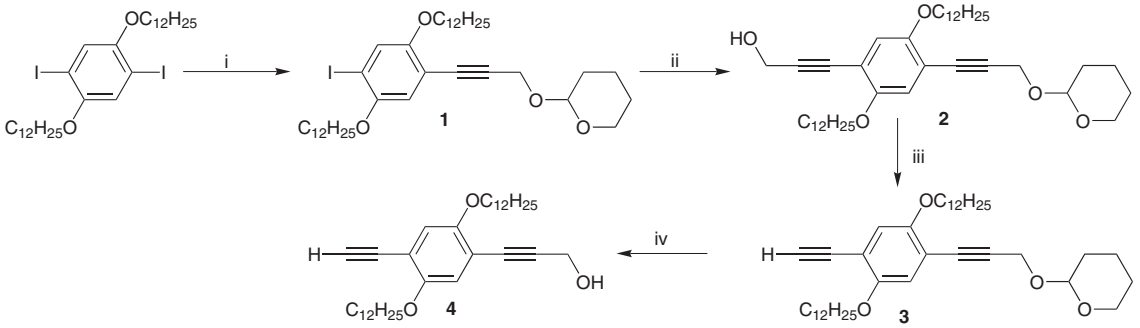
masking group. Furthermore, we have extended the application of this protecting group by converting the hydroxyl functionality to the corresponding tetrahydropyranyl (THP) ether as well. For example, tetrahydro-2-(2-propynyloxy)-2*H*-pyran was used as the staring material to achieve the preparation of compound **2** carrying two differently masked acetylene functionalities. When treated with mild acid (*p*-TsOH), the THP linkage in compound **4** was readily removed and the corresponding hydroxymethyl moiety was easily regenerated (Scheme 1).

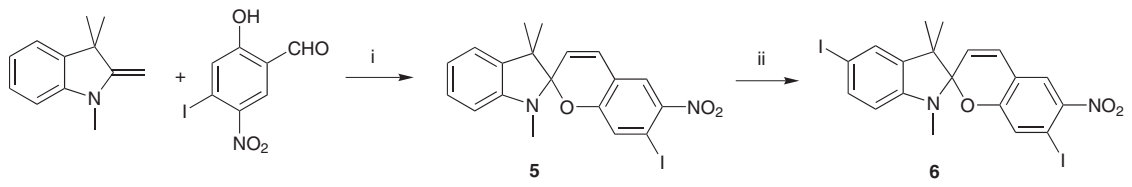
A selective mono-cross coupling reaction of 1,4-bis(dodecyloxy)-2,5-diiodobenzene (> two-fold excess) with tetrahydro-2-(2-propynyloxy)-2*H*-pyran under typical Sonogashira conditions provided monoiodo acetylene **1** in reasonable yield (61%). This compound was further subjected to another cross-coupling with excess propargyl alcohol to give bis(acetylene) **2** having different protecting groups on the two acetylene moieties. The hydroxymethylethynyl masking group was then removed by stirring a solution of compound **2** with a mixture of powdered manganese dioxide and potassium hydroxide in diethyl ether at room temperature to yield terminal acetylene **3**. Compound **4** was then obtained upon further treatment of **3** with catalytic amounts of *p*-toluenesulfonic acid (PTSA) in dichloromethane and methanol (2:1). 7-Iodo-6-nitro-5′-iodospirobenzopyran **6** was readily available from the condensation of commercially available 1,3,3-trimethyl-2-methyleneindoline with 4-iodo-5-nitrosalicylaldehyde,[9] followed by iodination with benzyltriethylammonium dichloroiodate ($BnEt_3NICl_2$) as shown in Scheme 2.[10]

A two-fold cross-coupling reaction of diiodide **6** with acetylene alcohol **4** afforded **7** in 59% yield. Removal of the hydroxymethyl moiety by manganese dioxide and potassium hydroxide afforded bis(acetylenic) monomer **8** in 62% yield (Scheme 3). The polymerization of **8** with 1,4-diiodobenzene was catalyzed by $Pd(PPh_3)_2Cl_2$ and CuI in a mixture of toluene and triethylamine (Scheme 4). The polymerization was allowed to run at room temperature for 48 hours before it was quenched with a saturated aqueous ammonium chloride solution. The crude polymer was purified by repeated precipitation of a concentrated dichloromethane solution of the polymer from methanol. The purified polymer was determined to have a molecular weight (M_w) of 24,272 by gel permeation chromatography (GPC) analysis, with a polydispersity index (PDI) of 1.23.

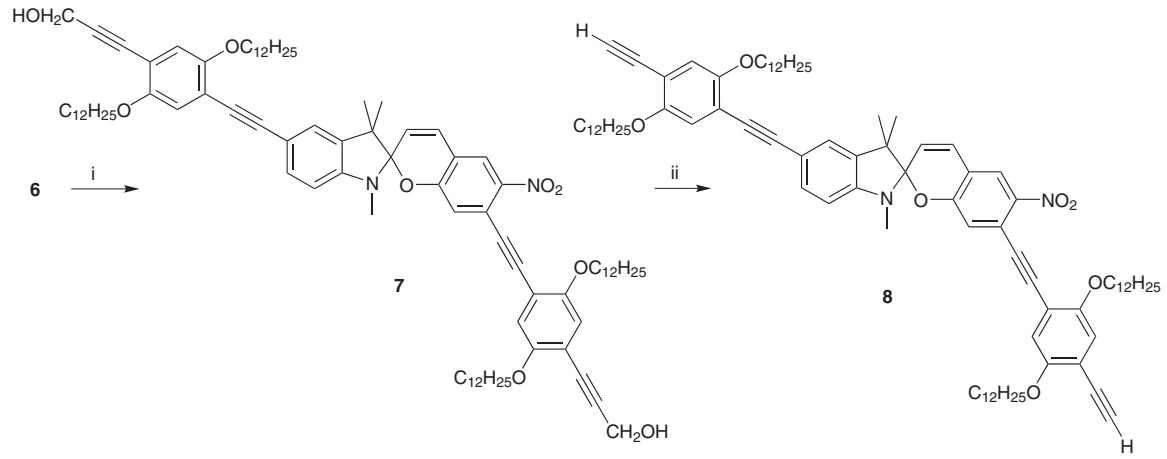
Figure 1 shows the UV-Vis absorption spectra of the polymer **9** (0.01 mg/mL) in chloroform. Upon irradiation with UV light of 365 nm, a new absorption band appeared above 500 nm due to the formation of the merocyanine form which bridges the conjugated systems between two adjacent ethynylphenyl moieties (Scheme 5). In addition, the absorption bands at 397 nm and 315 nm in the closed-ring PPE polymer were slightly blue-shifted to 388 nm and 309 nm, respectively, as a result of the ring-opening isomerization reaction. Overall the signal changes appear to be relatively small which may point to the fact that relatively few spirobenzopyran units undergo ring-opening isomerization upon irradiation. The general difficulty encountered in the isolation of unstable merocyanine form of the polymer has also precluded the determination of the extinction coefficient of the appropriate functionality that could quantify the degree of ring opening in the present system. In summary, a new photochromic polymer with spirobenzopyran units incorporated in the PPE backbone was synthesized. Future studies will focus on optimization of the photochromic properties by fine-tuning the electronic and optical properties of the substituent on the conjugated system.



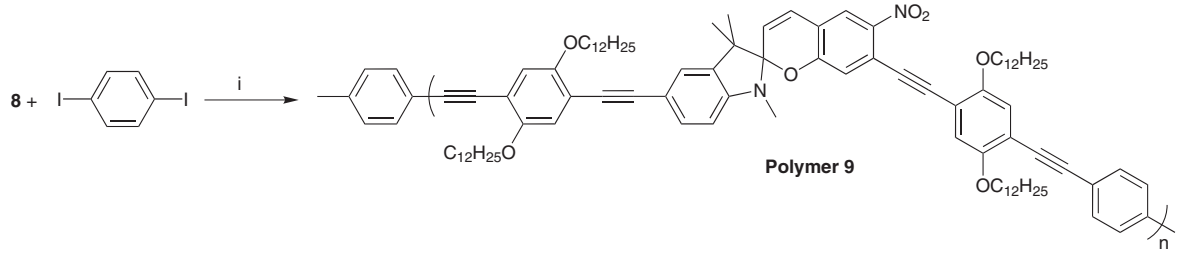
Scheme 1 Synthesis of terminal acetylene **4**. *Reagents and conditions*: (i) Tetrahydro-2-(2-propynyloxy)-2*H*-pyran, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (ii) propargyl alcohol, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (iii) MnO_2, powdered KOH, Et_2O, r.t.; (iv) PTSA, CH_2Cl_2, MeOH, r.t.



Scheme 2 Synthesis of diiodospirobenzopyran **6**. *Reagents and conditions*: (i) EtOH, reflux; (ii) $BnEt_3NICl_2$, $CaCO_3$, CH_2Cl_2, MeOH.



Scheme 3 Synthesis of bis(acetylene) monomer **8**. *Reagents and conditions*: (i) **4**, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, toluene; (ii) MnO_2, KOH, Et_2O, r.t.

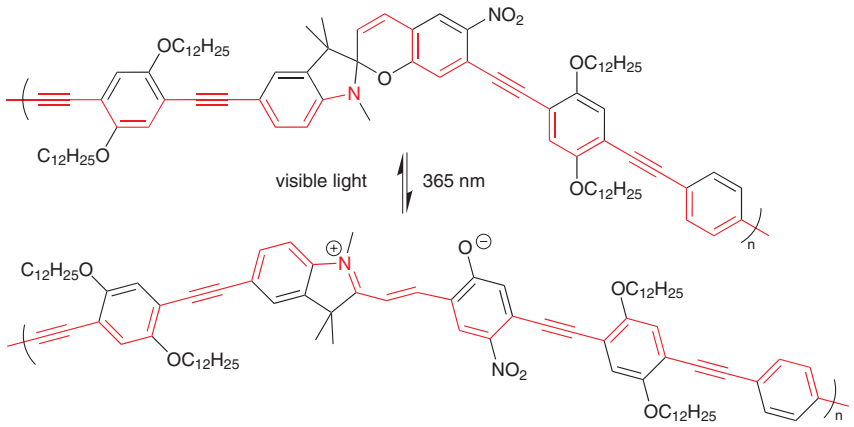


Scheme 4 Synthesis of polymer **9** by palladium-catalyzed polymerization of monomer **8** with 1,4-diiodobenzene. *Reagents and conditions*: (i) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, toluene.

All reagents and solvents were obtained from commercial suppliers unless otherwise noted. All cross-coupling reactions and other air-sensitive reactions were performed under a nitrogen (or argon) atmosphere. ^1H NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer at 400 MHz. ^{13}C NMR spectra were recorded on a Bruker Avance-500 NMR spectrometer at 100 MHz. HRMS data were obtained at the Washington University Mass Spectrometry Resource using the ESI technique.

Compound 1

To a solution of 1,4-bis(dodecyloxy)-2,5-diiodobenzene (29.0 g, 41.5 mmol), $Pd(PPh_3)_2Cl_2$ (60 mg, 0.085 mmol) and CuI (32.6 mg, 0.17 mmol) in toluene (100 mL) and Et_3N (30 mL), was added dropwise a solution of tetrahydro-2-(2-propynyloxy)-2*H*-pyran (2.40 g, 17.12 mmol) in toluene (10 mL) over a period of 1 h at r.t. under a nitrogen atmosphere. The reaction mixture was stirred for an additional hour and then poured into H_2O and extracted with Et_2O. The aqueous layer was further extracted with Et_2O. The combined organic extracts were washed with H_2O, brine and dried over anhyd Na_2SO_4. The solvent was evaporated on a rotary evaporator under reduced pressure and the solid residue was chromatographed on a silica gel column (hexane–CH_2Cl_2, 5:1 → 1:2) to afford **1** (yield: 7.45 g, 10.48 mmol, 61%) as a white solid; mp 34–35 °C.



Scheme 5 Linear spirobenzopyran-functionalized π-conjugated polymer with segmented conjugation (SP form) and fully extended conjugation (MC form) in different photoisomerizable states.

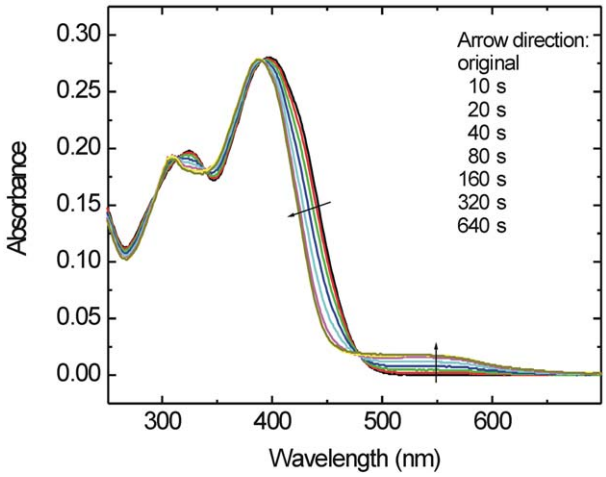


Figure 1 UV–Vis absorption spectra of polymer **9** upon irradiation with UV light at 365 nm (arrow indicates changes in spectral response upon initial UV irradiation).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (s, 1 H), 6.83 (s, 1 H), 4.93 (t, *J* = 3.3 Hz, 1 H), 4.45–4.55 (m, 2 H), 3.90–3.95 (m, 4 H), 3.85–3.89 (m, 1 H), 3.53–3.58 (m, 1 H), 1.26–1.88 (m, 46 H), 0.88 (t, *J* = 6.8 Hz, 6 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{38}H_{63}O_4I$: 733.3669; found: 733.3646.

Compound 2

The synthetic procedure of **2** is similar to that of **1**; yield: 85%; mp 61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (s, 1 H), 6.89 (s, 1 H), 4.94 (t, *J* = 3.3 Hz, 1 H), 4.57 (s, 2 H), 4.47 (s, 2 H), 3.91–3.96 (m, 4 H), 3.85–3.88 (m, 1 H), 3.54–3.57 (m, 1 H), 1.74–1.89 (m, 7 H), 1.54–1.68 (m, 4 H), 1.41–1.47 (m, 4 H), 1.26–1.30 (m, 32 H), 0.88 (t, *J* = 6.8 Hz, 6 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{66}O_5$: 661.4808; found: 661.4797.

Compound 3

To a solution of **2** (1.15 g, 1.80 mmol) in Et_2O (20 mL) was added KOH powder (1.01 g, 18.0 mmol) and MnO_2 (3.13 g, 36.0 mmol). The mixture was stirred at r.t. for 2 h and then filtered through a short pad of silica gel, eluted with Et_2O to afford **3** (yield: 1.06 g, 1.74 mmol, 97%) as a light yellow solid; mp 53–54 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 1 H), 6.91 (s, 1 H), 4.94 (t, *J* = 3.1 Hz, 1 H), 4.48–4.56 (m, 2 H), 3.92–3.97 (m, 4 H), 3.86–3.91 (m, 1 H), 3.55–3.57 (m, 1 H), 3.31 (s, 1 H), 1.26–1.87 (m, 46 H), 0.88 (t, *J* = 6.8 Hz, 6 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{40}H_{64}O_4$: 632.4736; found: 632.4734.

Compound 4

A solution of **3** (0.50 g, 0.82 mmol) and *p*-toluenesulfonic (PTSA) monohydrate (31.2 mg, 0.164 mmol) in CH_2Cl_2 (10 mL) and MeOH (5 mL) was stirred at r.t. until all of the starting material was consumed as monitored by TLC analysis. The resulting solution was poured into sat. aq $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, brine and dried over anhyd Na_2SO_4. The solvent was removed in vacuo to afford the desired product as a white solid (yield: 0.40 g, 0.76 mmol, 92%); mp 68–69 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (s, 1 H), 6.91 (s, 1 H), 4.53 (s, 2 H), 3.95 (m, 4 H), 3.32 (s, 1 H), 1.79 (m, 4 H), 1.45 (m, 4 H), 1.26–1.36 (m, 33 H), 0.88 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 153.3, 117.8, 117.2, 113.7, 112.8, 92.6, 82.3, 81.8, 79.8, 69.7, 69.6, 51.8, 31.9, 29.7, 29.6, 29.6, 29.3, 29.1, 25.9, 25.9, 22.7, 14.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{56}O_3$: 548.4161; found: 548.4156.

Compound 5

To a suspension 2-hydroxy-4-iodo-5-nitrobenzaldehyde (1.50 g, 5.12 mmol) in EtOH (30 mL) was added a solution of 1,3,3-trimethyl-2-methyleneindoline (887 mg, 5.12 mmol) in EtOH (30 mL). The resulting mixture was heated to 65 °C for 3 h. Excess solvent was removed in vacuo and the solid residue was chromatographed on a silica gel column (hexane–CH_2Cl_2, 3:1 → 2:1) to afford the desired product as a yellow solid (yield: 0.80 g, 1.785 mmol, 34%); mp 150 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.40 (s, 1 H), 7.21 (t, *J* = 7.7 Hz, 1 H), 7.09 (d, *J* = 7.2 Hz, 1 H), 6.87–6.91 (m, 2 H), 6.56 (d, *J* = 7.7 Hz, 1 H), 5.89 (d, *J* = 10.3 Hz, 1 H), 2.74 (s, 3 H), 1.30 (s, 3 H), 1.18 (s, 3 H).

Compound 6

Compound **5** (800 mg, 1.785 mmol) was dissolved in CH_2Cl_2 and to the solution were added successively $BnEt_3NICl_2$ (1000 mg, 2.56 mmol) and $CaCO_3$ (367 mg, 3.67 mmol). The resulting mixture was stirred at r.t. for 24 h. Excess $CaCO_3$ was removed by filtration and the filtrate was poured into H_2O and washed with aq sodium bisulfite, H_2O, and brine, then dried over anhyd Na_2SO_4. Excess solvent was removed in vacuo and the solid was purified by column chromatography (silica gel; hexane–EtOAc, 4:1 → 3:1) to afford the desired product as a yellow solid (yield: 0.65 g, 1.13 mmol, 63%); mp 175 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1 H), 7.48 (dd, *J* = 1.7, 8.2 Hz, 1 H), 7.40 (s, 1 H), 7.32 (d, *J* = 1.7 Hz, 1 H), 6.89 (d, *J* = 10.3 Hz, 1 H), 6.34 (d, *J* = 8.2 Hz, 1 H), 5.85 (d, *J* = 10.3 Hz, 1 H), 2.70 (s, 3 H), 1.26 (s, 3 H), 1.17 (s, 3 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}N_2O_3I_2$: 574.9329; found: 574.9332.

Compound 7

A mixture of compound **6** (50 mg, 0.087 mmol), **4** (114 mg, 0.217 mmol), $Pd(PPh_3)_2Cl_2$ (2.4 mg, 0.0034 mmol) and CuI (0.7 mg, 0.00348 mmol) in toluene (3 mL) and Et_3N (2 mL) were stirred at r.t. for 30 min and then heat to 50 °C overnight. The mixture was poured into sat. aq NH_4Cl solution. The organic layer was washed with H_2O, brine and dried over anhyd Na_2SO_4. Excess solvent was removed in vacuo and the residue was chromatographed on a silica gel column (hexane–EtOAc, 4:1 → 3:1) to afford the desired product as a thick brown oil (yield: 70 mg, 0.0511 mmol, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.39 (d, *J* = 7.9 Hz, 1 H), 7.23 (s, 1 H), 6.96–6.98 (m, 3 H), 6.90–6.93 (m, 3 H), 6.49 (d, *J* = 8.1 Hz, 1 H), 5.85 (d, *J* = 10.3 Hz, 1 H), 4.52 (s, 2 H), 4.51 (s, 2 H), 3.93–3.99 (m, 8 H), 2.75 (s, 3 H), 1.74–1.86 (m, 8 H), 1.39–1.62 (m, 8 H), 1.18–1.34 (m, 72 H), 0.82–0.87 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 154.0, 153.5, 153.4, 153.2, 147.7, 141.8, 136.2, 132.1, 128.0, 124.9, 124.0, 121.7, 121.0, 120.3, 118.4, 117.4, 117.3, 117.2, 116.6, 115.0, 114.3, 114.1, 113.2, 112.3, 106.8, 105.9, 96.1, 94.5, 93.1, 92.3, 90.6, 83.9, 82.1, 81.9, 69.6, 69.5, 52.1, 51.8, 51.7, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 29.1, 29.0, 28.7, 26.0, 25.9, 25.8, 25.8, 22.6, 19.9, 14.1.

Compound 8

Compound **7** (300 mg, 0.22 mmol) was dissolved in Et_2O (20 mL). To the resulting solution were added KOH powder (129 mg, 2.30 mmol) and MnO_2 (400 mg, 4.60 mmol). The mixture was stirred at r.t. overnight and then passed through a short pad of silica gel, and eluted with Et_2O. Excess solvent was removed in vacuo to afford the desired product (yield: 180 mg, 0.137 mmol, 62%) as a thick brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 7.24 (s, 1 H), 6.93–7.00 (m, 6 H), 6.51 (d, *J* = 8.1 Hz, 1 H), 5.87 (d, *J* = 10.3 Hz, 1 H), 3.97–4.02 (m, 8 H), 3.35 (s, 1 H), 3.33 (s, 1 H), 2.77 (s, 3 H), 1.77–1.87 (m, 8 H), 1.20–1.57 (m, 78 H), 0.85–0.89 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 154.2, 154.0, 153.9, 151.1, 147.8, 141.9, 136.2, 132.2, 128.1, 125.0, 124.0, 121.8, 121.0, 120.4, 118.5, 117.8, 117.7, 117.2, 116.6, 115.4, 114.1, 113.8, 113.6, 111.8, 106.8, 105.9, 96.2, 94.5, 90.7, 83.9, 82.8, 82.0, 80.1, 79.9, 69.7, 69.6, 69.6, 52.1, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 28.8, 26.1, 25.9, 25.9, 22.7, 19.9, 14.1.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{87}H_{122}N_2O_7$: 1307.9330; found: 1307.9271.

Polymer 9

Compound **8** (143 mg, 0.109 mmol) and 1,4-diiodobenzene (36 mg, 0.109 mmol) were dissolved in toluene (2 mL) and Et_3N (1 mL). To the solution were added $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol) and CuI (0.8 mg, 0.004 mmol). The reaction mixture was stirred at r.t. for 48 h under a nitrogen atmosphere. The solution was poured into sat. NH_4Cl solution and the organic layer was separated. The aqueous layer was further extracted with Et_2O. The combined organic layer was washed with H_2O, brine and dried over anhyd Na_2SO_4. The solution was concentrated to a small volume and MeOH was added slowly to precipitate the polymer.

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